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FINAL TECHNICAL REPORT

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THE RELATIONSHIP OF STRUCTURE AND PROPERTIES TO DEPOSITION CONDITIONS AND THE ORIGIN OF RESIDUAL STRESS IN CVD SILICON CARBIDE AND NITRIDE

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FEBRUARY 13, 1981

ABSTRACT

Two limiting factors in the acceptance of CVD SiC as a structural material have been deposition control and residual stress in the deposit. Deposition parameters have been related to morphological as well as crystallographic structures. The effect of various additions to the basic methyltrichlorosilane and hydrogen deposition gases has also been studied and the effect on structure noted. Deposition rate control through the interaction of these parameters has also been obtained. Residual stresses large enough to crack deposits have been observed. Although no quantitative model has been determined to predict these stresses, a qualitative model has been proposed which allows the trends in residual stress to be predicted. This model is based on structure. Finally, the strength of CVD SiC was determined using a biaxial tensile test to obtain a closer approximation of the as-deposited strength than is possible with three or four-point bend tests.

INTRODUCTION

Silicon carbide is a candidate material for high-temperature sections of energy conversion devices. Its attractiveness results from a combination of high strength at elevated temperatures, high modulus, good thermal conductivity, relatively low thermal expansion and excellent oxidation resistance to temperatures of 1600°C. Since high structural integrity is necessary for such devices, materials forming options are needed which do not introduce strength-reducing flaws. These include chemical vapor deposition (CVD), hot-pressing, and sintering. CVD is under study since high purity, theoretically dense, controlled microstructure material may be deposited directly to the desired form. Sintering and hot-pressing require the addition of sintering aids which decrease high-temperature properties. Machining, with the resultant strength-reducing flaws, is also often not required with CVD materials. Gulden[1] has measured the strength of very small pieces of silicon carbide (.040° wide x .004" thick x .062" outer gauge length) using 4-pt. bend tests. He found the strength to be relatively constant from room temperature to 940°C and in the range of from 106,000 to 144,000 psi. A general increase to the range from 134,000 to 189,000 psi was observed as temperature was increased to 1400°C. For CVD SiC deposited at R.P.I., Weiss[2] has reported an average room temperature strength of 48,000 to 72,000 psi for larger specimens. Testing to 1400°C increased the average strength to 80,000 psi, while testing at 1500°C resulted in a 180,000 psi average strength. Breaking at room temperature after heating to 1400°C in air resulted in increasing room temperature strength to 80,000 psi. These values demonstrate the excellent high temperature strength possible with CVD SiC. Creep was not measureable at 1550°C, an applied load of 30,000 psi, and a machine sensitivity of better than 10^{-9} per second.

DIRECTION OF WORK

Given these advantages, what limiting factors prevent the use of CVD SiC? Cost has been traditionally high, primarily because little scientific knowledge has been used to determine the best set of deposition parameters to form the material with the desired structure and deposition profile. In addition, stresses are developed in the deposits which range from several thousand psi, which reduce the useful strength of the deposit, to those causing fracture of the ma... ial. These factures have been observed both during deposition and upon cool-down of the system. These two areas are the primary targets for this research.

DEPOSITION CONTROL

Chemical vapor deposition is a molecular forming process where a gas or gases containing the desired deposit atoms are passed over a heated substrate and form the desired material. The reaction is in general endothermic. CVD as a process is theoretically less well understood than physical vapor deposition where fundamental variables such as supersaturation may be more definitely specified. However, certain concepts relevant to any nucleation and growth process are still valid. The number of nucleation sites should increase as the supersaturation of the system increases. The analysis of this step for a CVD system is more complex, however, as more than one species is in general participating in the deposition process which makes a simple definition of supersaturation difficult. Also, substrates are in general less than perfect, and surface defects and impurities which act as nucleation sites are very prevalent. Chemical reaction of the depositing species to form the nucleus also complicates nucleation calculations. Figure 1 illustrates the difficulties. Shown are the first-deposited surface of two specimens deposited under nominally

equal conditions. Very different nucleation densities have resulted, but whether they are from substrate differences or initial fluctuations in growth conditions is not clear.

Growth from these nuclei is controlled by several processes, any of which can be rate-limiting. For the CVD of SiC, (1) the methyltrichlorosilane (MTCS) must be decomposed in the region adjacent to the substrate, (2) the resulting reactive species must be transported to the substrate surface, (3) these species must be adsorbed and then diffuse and react, (4) product species must be then desorbed and finally transported away. MTCS is the precursor most commonly used in the CVD of SiC because of its relative ease of handling, availability, and one to one carbon to silicon ratio. Figure 2 illustrates schematically the steps in the growth process for the formation of SiC from MTCS. Maximum deposition rate will be achieved when mass transport is the controlling step (high reactant flux), while uniform deposition over an extended substrate is best achieved when surface kinetics are controlling (generally low temperature).

Thermodynamic calculations can determine the equilibrium gas phase composition. However, due to changing temperature and concentration profiles as the gas flows in the tube, it must be kept in mind that these are only the best thermodynamic estimate as to the actual species present. Using the free energy minimization technique as outlined by Oliver[3] for the determination of equilibrium gas phase composition, the predominant gas phase species were determined to be C_2H_2, $SiCl_2$, H_2, and HCl for typical deposition conditions used here at R.P.I. The fact that $SiCl_2$ is the predominant silicon containing species is important in that its presence is one of the reasons why hydrogen has been found necessary for

the deposition of pure SiC. Thermally decomposing MTCS alone or with an inert gas gives rise to severe nucleation problems as well as the deposition of free graphite. This was determined initially by Popper[4] and since confirmed by many researchers. Cartwright[11] has theorized a decomposition of MTCS as shown in Figure 3. He notes that the carbon-silicon bond is the weakest in the compound, and therefore the first to break as the molecule is heated. $SiCl_2$, a stable molecule, is theorized to be the silicon reactive species. Excess hydrogen is required to reduce this molecule so that silicon is available for the deposition of SiC. Excess hydrogen also inhibits the decomposition of methyl radicals which would result in excess carbon or pyrolytic graphite deposition. Since carbon and silicon are depositing independently, an input ratio of one carbon to one silicon atom is not sufficient to insure the deposition of stoichiometric silicon carbide. The ability of the gas phase to absorb excess silicon or carbon by the formation of silicon chlorides or methyl radicals which are thermodynamically stable in the vapor phase will also inhibit excess carbon or silicon deposition.[5A]

Various additions to the system have been examined at R.P.I. Silicon tetrachloride was used in an attempt to improve high temperature deposits. At higher temperatures, silicon incorporation into the deposit becomes increasingly difficult as its relative supersaturation decreases. Though the maximum deposition rate decreased somewhat, where excess carbon or poor nucleation had been a problem, the deposits obtained with the $SiCl_4$ addition were good silicon carbide. The addition of HCl to inhibit excess silicon deposition at low temperatures by forming gas phase silicon chlorides was also attempted. Large amounts of HCl at 1350°C completely halted deposition while smaller amounts led to the formation of closely spaced islands of SiC. These results indicate

that the gas phase composition for the production of good SiC is very close to that currently being used (H_2:MTCS ≈ 2:1).

Acetylene and methane were added to study their effect on composition as well as structure. It was hoped that a continuously nucleated material could be produced with excess carbon in the system so that the typical growth cone structure could be avoided. This was not successful. At the upper temperature limit where good SiC is formed, an acetylene addition resulted in pyrolytic graphite formation with only a few scattered islands of SiC. Lower temperatures produced a powdery deposit. A methane addition gave a very smooth deposit compared to one without methane, but growth cones still extended through the thickness of the deposit.

The particular furnace system used at R.P.I. is schematically shown in Figure 4. It consists of a resistance heated graphite which radiantly heats the graphite substrate through which the reactive gas mixture is fed through. Gas flow is controlled by rotameters or mass flow controllers. The entire system is operated at reduced pressure (typically five to ten mm Hg) to avoid gas phase nucleation from high supersaturation. This is the alternative to operating at atmospheric pressure where an inert dilutent gas such as argon must be added. Temperature is measured by an optical pyrometer. The system design is what is known as a "hot-wall reactor". The other option is the "cold-wall reactor" where the gas is passed by a resistance heated rod or wire. This introduces large thermal and concentration gradients in the gas which are eliminated in the "hot-wall" configuration. The gas temperature and concentration of reacting species both reach steady-state values after an initial period during which the gas is being heated to deposition temperature and reactive

species formed. Further down the tube the concentration of reactant decreases as it is stripped by deposition. These idealized profiles are illustrated in Figure 5 which also shows the resulting characteristic deposition profile.

The effect of varying deposition parameters on both structure and deposition profile has also been analyzed. Weiss[2] has measured deposition profiles as single parameters were varied. As an example Figure 6 shows that increasing deposition temperature shifts the maximum in deposition rate towards the inlet. Increasing the flow rate flattens the deposition profile as does higher initial concentrations of MTCS. The use of other reactants will also have an effect on the deposition profile as illustrated in Figure 7 where methyldichlorosilane has been substituted for MTCS. Here the shift in deposition maximum is due to less chlorine in the system allowing silicon to be incorporated in the deposit as opposed to various gas-phase silicon chloride compounds.

Knowledge and control of the resulting microstructure is also important. A scanning electron microscopy study of morphological features for various deposition parameters was undertaken. The surface morphology can be interpreted in terms of how the deposit is forming. The effect of temperature is shown in Figure 8. At 1000X, the crystal features of the high temperature deposit cover the entire field of the photograph while the lower temperature deposit has features orders of magnitude smaller. This difference is due to the decreased surface mobility of atoms during deposition at the lower temperatures.

The effect of gas phase composition can be seen in Figure 9. At 1000X, a deposit formed with 33% reactant vs. 11% is much less crystalline as surface rearrangement time is decreased at the resultant higher deposition rates.

Finally, the effect of pressure is seen in Figure 10 at 50X where at higher pressures the material exhibits deeper crevices between growth nodules. The sharper concentration gradient at higher pressure causes any protuberance to grow into the richer gas stream away from the deposit surface. This is also an indication that the growth of SiC in this system is at least partially diffusion rate limited.

Crystallographically, SiC is polytypic. This is a special form of polymorphism, where though the structure is the same in two dimensions, it varies in the third. Silicon carbide is formed by the close-packing of tetrahedrally coordinated, predominantly covalently bonded layers of silicon and carbon. The strong directional bonding is responsible for the high hardness, melting point and strength of pure SiC. Verma and Krishna[5] have written a book discussing polytypism with an extensive review on the theories relating to SiC. Knippenberg[6] studied both the growth and structure of SiC extensively, though primarily in its single crystal form. Any structure can be specified by stating the position of the close-packed planes; either A, B, or C just as in close-packed metals. However, one close-packed layer actually represents two combined atom layers, one silicon and one carbon. The cubic stacking sequence, ABCABC, is the β form of SiC while all other non-cubic forms are termed α. Approximately one hundred non-cubic forms have been identified, with repeating stacking sequences ranging from two to several hundred.[7] The observation that these long period polytypes exist can be roughly understood from the fact that, as nearest-neighbor interactions are the same for all polytypes, the total energy to a first approximation does not depend on stacking order. However, no one has yet been able to formulate a comprehensive predictive theory for polytype formation. Pure polytypes are

exceedingly difficult to grow. Sato[8] has determined the stacking order in CVD SiC to be nearly random in the direction perpendicular to the close-packed planes.

Through analysis of x-ray diffractometer scans the relative amounts of cubic and non-cubic material as a function of temperature have been determined at R.P.I. as shown in Figure 11. The minimum amount of non-cubic material probably represents for this system the closest set of conditions for which pure cubic SiC can be formed. At temperatures above this, true on-cubic material is probably formed in accordance with the general trend to non-cubic SiC at high temperatures. At lower temperatures, the non-cubic material is probably disordered silicon carbide, there not being sufficient thermal energy for the atoms to reach the lowest energy state which appears to tend toward cubic material.

RESIDUAL STRESS

The motivation for the study of residual stress in CVD SiC comes from the resultant degradation of mechanical properties of the deposit, during or after completion of deposition. Stresses in CVD SiC are not an isolated case, they occur in nearly all atomically deposited materials with resultant degradation of optical, chemical, electrical, magnetic and mechanical properties. These stresses vary from near zero to high enough to cause fracture, spalling, or delamination of the deposit. Residual stresses in electrodeposits and thin films have been explained and characterized to a certain degree, but there is still no all inclusive theory which explains all observations. CVD systems with the exception of pyrolytic graphite, which is not typical because of its high anisotropy, have been even more poorly characterized. Experimental evidence, possible mechanisms, and what is believed to be the most applicable to CVD SiC will be discussed

in this section of the report.

Residual stresses have been noted by several researchers in CVD SiC. Weiss[2] studied the phenomena for a range of parameters and concluded a surface tension and crystallite boundary theory best explained his experimental evidence. He also found that increases in residual stress correlated best with increases in deposition rate.

Airey[9] characterized CVD SiC deposited on the outside of a thin, slit, graphite tube. Compressive stresses were developed which after an initial thin layer (70 microns) reached a relatively constant value. As soon as deposition was halted, further narrowing of the slit was not observed. This indicates stresses are developed during deposition and are not a result of cool-down. Lloyd[10] found for deposition on large tubes, no consistent pattern of residual stress sign for either internal or external deposits. Cartwright[11] for deposition on heated rods again found no single sign for stresses developed, though he associated high H_2:MTCS ratios with compressive stresses and high flow rates with tensile stresses in the coating. Crane[12] found the outer surface of SiC deposited on tungsten fibers to be in a slight tensile state. Gebhardt[13] found compressive residual stresses in internal CVD Si_3N_4 deposits. He correlated greater stresses with longer gas residence times. Engdahl[14] for CVD SiC formed at 1/3 atmospheric pressure found residual stress to have no relation with structure, but seemingly with impurities in the gas phase. Kamins[15] observed deformation during deposition of polycrystalline silicon. It was sporadic in nature, seemingly not an intrinsic material property. He related stresses to oxygen impurities inhibiting surface diffusion.

Possible explanations for stress in CVD SiC follow. The residual stress of interest is intrinsic, not simply a mismatch between either

the thermal expansion coefficient or lattice parameter of the substrate and deposit. Evidence for this is the observed popping off of deposits during a run as well as the bowing at temperature of a deposit to which excess silicon had been added. Thus, growth type stresses are predicted to be the primary contributor to residual stress in CVD SiC.

Thermal stresses, however, are a possible explanation. These would arise from the last deposited surface being at a lower temperature than the first deposited surface, either from cooling by the reactant gas which may not have reached deposition temperature or by cooling from the endothermic deposition reaction. Though no observable difference in temperature has been measured, it may still exist over a very few atomic layers. Upon cool-down, this would put the last deposited surface in compression and the first deposited surface in tension.

An excess energy theory detailed by Hoar and Arrowsmith[16] explains the origin of stresses with a model of surface atoms having a higher energy than the bulk. This would be of little importance in thick deposits, and as pointed out by Powell[17] is probably more applicable to deposits formed by methods other than CVD such as sputtering where the impinging atoms have a much greater energy.

Phase changes and the resultant volume change would also introduce stress. As outlined, SiC has polytypic structure related to undefined deposition variables. Using Gomes-De Mesquita's crystallographic data, the difference in volume between the two most extreme structures would be less than 0.1%.[18] This would not produce stresses of the magnitude necessary to fracture the material as has been observed. It may, however, vary the magnitude of observed stresses as different variables result in varying amounts of cubic material.

Hydrogen stresses are important in many systems, especially electrodeposits. Hydrogen is used in the deposition process in large quantities. However, the lowest stresses are found when the highest ratio of hydrogen is used, though the structure is radically different. Causey[19] has determined the solubility of deuterium at 1200°C in SiC and found it to be approximately 4×10^{-4} deuterium per silicon atom and decreasing with increasing temperature. This implies the amount of hydrogen in deposits is very small.

Diffusion stresses would include elimination of lattice dislocations, vacancies, or other defects from a deposit. Klokholm and Berry[20] theorized such an effect for evaporated metal films. The growth layer would not be fully dense if atoms did not have sufficient time to diffuse to equilibrium positions prior to being buried by the atomic layer of the deposit. Subsequent annealing to a denser structure will introduce tensile stresses in the deposit. The very low creep rate found for CVD SiC as well as its high melting or dissociation temperature indicate that atomic mobility within the deposit is quite limited at deposition temperature. As pointed out by Kamins[15], a possible mechanism leading to a decreased mobility of the depositing atoms would be incorporation of impurity atoms such as oxygen into the growth front. This would lead to a less ordered structure than would be possible in the absence of the impurity.

As detailed by Powell[17], anisotropy may also lead to stresses. In amorphous or polycrystalline material, local stresses have small magnitudes and tend to cancel out due to random structure. However, CVD materials tend to deposit with a definite preferred orientation, leading to a "growth anisotropy" preventing neutralization of local stresses. Other features which would introduce anisotropy would include any systematic variation in crystal size, material composition, or density of lattice vacancies,

inclusions, or dislocations. The large anisotropy of pyrolytic graphite in conjunction with actual growth of the deposit during deposition is one of the extreme examples of this phenomena leading to large residual stresses. Baratta[21] has derived equations for stresses arising on cool-down of an anisotropic material in cylindrical form. For typical deposition conditions and geometries used here at R.P.I., a compressive stress of approximately 4,000 psi is calculated for the first deposited surface. Though this may add a constant value to determined room temperature stresses, it is not large enough to account for observed values.

A defect theory has been proposed by Popereka[22] for electrodeposits. Since all deposited layers are formed under similar conditions, usually with a pronounced growth direction, dislocations of one sign will predominate in crystals of a deposit. If dislocations were free to move, the repulsion of similar dislocations would cause them to move to surfaces and disappear causing a reduction in volume in the deposit and resultant tensile stress. Though CVD SiC deposits atomically as do electrodeposits, dislocations do not easily move, nor has there been a high density of dislocations observed.[23]

Hoar and Arrowsmith[16] combined this mechanism with various surface effects to explain stresses in electrodeposits. If excess vacancies exist at the surface, a situation as shown in Figure 12a would develop leading to a tensile stress in the material. If impurities were adsorbed on the surface as shown in Figure 12b, compressive stresses would result.

The model Weiss proposed[2] for CVD SiC was a combined surface tension and crystallite boundary mismatch one. There are several possibilities of how surface tension can contribute to residual stress. The first is that proposed by Hoar and Arrowsmith.[16] They theorized that for rapidly deposited electrodeposits, equilibrium would not be reached and each layer after being buried by the next depositing layer may retain some of the

surface tension associated with a solid surface. As detailed by Powell,[17] there is also the possibility of a "quasi-liquid" phase existing at high temperatures in CVD deposits. This model is tentative at best due to the lack of knowledge of the stress state of liquids at high temperature and still less of solids at any temperature.

Stress from surface tension in a more conventional sense as shown by Chopra[24] would be:

$$\text{Stress} = \frac{\sigma_1 + \sigma_2}{t}$$

where σ_1 is the surface tension of the deposit-gas interface, σ_2 is the surface tension of the deposit-substrate interface, and t is the thickness of the film. This would be important only for much thinner deposits than are presently under observation.

Several researchers have formulated surface tension effects with crystallite mismatch effects[25,26] for electrodeposits. This is basically what Weiss has proposed for CVD SiC[2]. An initial compression is set up due to surface tension of the discrete muclei. As the nuclei become bonded to the substrate and grow laterally, tension is developed from attraction as well as the tendency to reduce surface area at grain boundaries. As Weil[25] points out, as grain size increases, stress should decrease due to less grain boundary area. However, larger grains also tend to have a higher degree of boundary mismatch leading to greater tensile stresses. What would therefore be expected is a tensile stress increasing to a continuous value as the deposit becomes continuous. Weiss[2] theorized a compressive stress in the first deposited surface due to surface tension of individual grains. As competitive growth proceeds between crystallites such as growth cone interfaces, further compressive stresses were theorized to develop. This compressive stress would decrease

as the growth cones became increasingly parallel. Powell[17] points out that surface tension or tension due to lattice vacancies and dislocations between cone shaped aggregates will have a horizontal component varying as the cosine of a normal to the substrate and the side of the growth cone. The magnitude will be greater on the substrate side due to smaller grains, but the cosine of the angle may be smaller at this point. Therefore, stresses from surface tension will reach a maximum close to, but not necessarily at the substrate interface.

Experimentally, residual stresses have been measured in several ways at R.P.I. A flat deposit was analyzed through its thickness for stress determination by analysis of the bending resulting from material removal on the last-deposited surface. The results are shown in Figure 13. As can be seen, a high compressive stress was found at the first deposited surface, consistent with the decreasing radius of curvature as material was removed. This is also consistent with the experimental observation that when tube-like deposits are slit in the longitudinal axis, the outside radius in general shows a decrease in dimension. However, very thick coarsely nucleated deposits formed upon flat plates have shown a tendency to have the first deposited surface in tension. Experimental evidence for this is open cracks at the first deposited surface of such deposits formed here at R.P.I.

While these statements may appear contradictory, Lloyd[10] also found inconsistency in the sign of the residual stresses in his deposits of SiC, though no explanation was offered. What appears to be occurring is that in addition to the stresses resulting from surface tension and crystallite mismatch, stresses arise from the competitive growth of the cone-like features of the deposit. The growth component parallel to the substrate

is inhibited by competing growth cones. However, since the reaction is at least partially diffusion rate limited growth cones exhibiting preferred growth directions will crowd out others. Finely nucleated deposits, as are generally formed in the 1" I.D. tubes used for most of the deposits at R.P.I., would be expected to have large compressive stresses at the first deposited surface followed by compressive stresses of decreasing magnitude. The final profile would show the first deposited surface in compression and the last in tension. Coarsely nucleated structure would show little stress at the first deposited surface followed by increasing compressive stress as the growth cones began to crowd each other out. The final stress profile would show the first deposited surface in tension with the last in compression. (See Figure 13A.)

Some experimental evidence for this is seen in Figure 14. The {111} preferred orientation can be thought of as a measure of orientation of these growth cones as the <111> direction is the preferred direction of CVD SiC. This finely nucleated structure took several mils to reach a nearly constant preferred orientation. Thus, a compressive stress at the first deposited surface would be expected. This is consistent with the fact that only in coarsely deposited material have tensile cracks appeared at the first deposited surface.

Additional evidence for this mechanism can be seen in Figure 15. This is a poorly nucleated sample, but what is important to notice is the spherical shape of the deposit which did form. In a deposit which nucleated evenly, as the nuclei attempted to gain this spherical shape, they would be inhibited by impringement with other nuclei. This would set up compressive stresses.

This is also consistent with the observation by Weiss[2] that residual stress levels correlated best with deposition rate. These high deposition

rates also tend to fine nucleation. Though his explanation is probably mechanically correct, it is not a true surface tension and crystallite boundary mismatch explanation. It would be better termed the preferential or competitive growth mechanism.

Using strain gauges as shown below, stress was measured in one-inch diameter tubes of material, approximately 200 mils thick. The most rapidly deposited material tested (1500°C, H_2/MTCS = 2:1; 6 CFH H_2) showed the highest residual stress, nearly 80,000 psi. The test configuration is shown in Figure 16.

Finally, using a biaxial test rig as shown in Figure 17, the strength of several pieces of silicon carbide prepared at R.P.I. was measured. This test rig was patterned after the one proposed by Wachtman.[27] It was thought that this type of measurement would provide a better feeling for the intrinsic value of strength of CVD SiC, as only a highly polished surface is subjected to the maximum tensile stress. This is different than three or four-point bend tests where the edges of the test samples often suffer from machining damage. Prior to testing, the samples were given a vacuum anneal at 1400°C for 15 minutes. The motivation for this heat-treatment was similar to that of Johnson,[28] that is to blunt surface cracks. In our experiment, it was not thought necessary to remove several μm of material, however. The goal was to blunt flaws that were nearly of an atomic level. Since the samples had taken several weeks to prepare, drastic annealing was deemed undesirable. The four specimens yielded strengths of 54, 74, 81 and 118 Kpsi. These samples were 1.1 inches in diameter and 50 mils thick. Several conclusions were made at the time using the Weibull modulus calculated. Although four samples is indeed a small sample size. However,

the most important conclusion which can be drawn from these results is that using the Weibull modulus calculated from previous tests of CVD SiC at R.P.I. as well as the volume of these samples— the predicted biaxial strength would have been 59,000 psi. The values obtained indicate that if CVD SiC can be formed directly to shape, eliminating the need for machining, higher strengths can be expected than predicted by bend tests.

CONCLUSIONS

(1) While varying deposition geometries will yield different results, the best results using MTCS and H_2 as the reactant gas will be obtained near 1450°C and a 2:1 MTCS/H_2 ratio. If the resultant deposit raises from the desired structure, the results of this work will give the proper direction for deposition condition changes to obtain the desired structure.

(2) The addition of excess chlorine to the system decreases deposition rate. This indicates that in the temperature range studied, the deposition of silicon is the rate-limiting step.

(3) Residual stress patterns were correlated with deposit structure. Coarsely nucleated material was found to be in tension at the first-deposited surface while finely nucleated material was in compression.

(4) The crystallographic structure of the material was studied. Since cubic and hexagonal structures are present in deposits in varying amounts, their relative amounts in relation to deposition conditions was studied. No correlation with residual stress was determined.

(5) Biaxial tensile testing of several samples of CVD SiC gave an average strength of about 82,000 psi. In relation to specimen size, this is somewhat higher than would be predicted from bend test data. It is probably a more realistic value for intrinsic strength of CVD SiC prior to machining.

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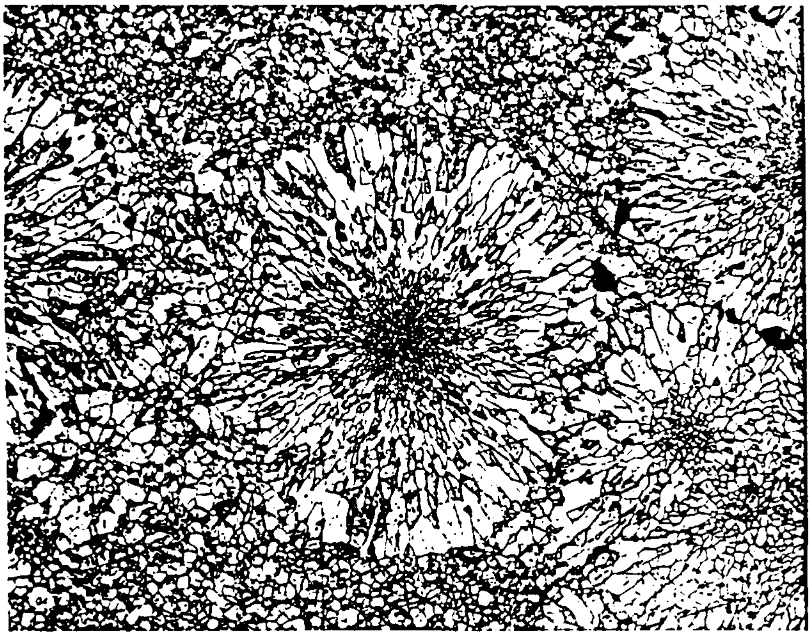
Figure 1 Coarse vs. Fine Nucleation

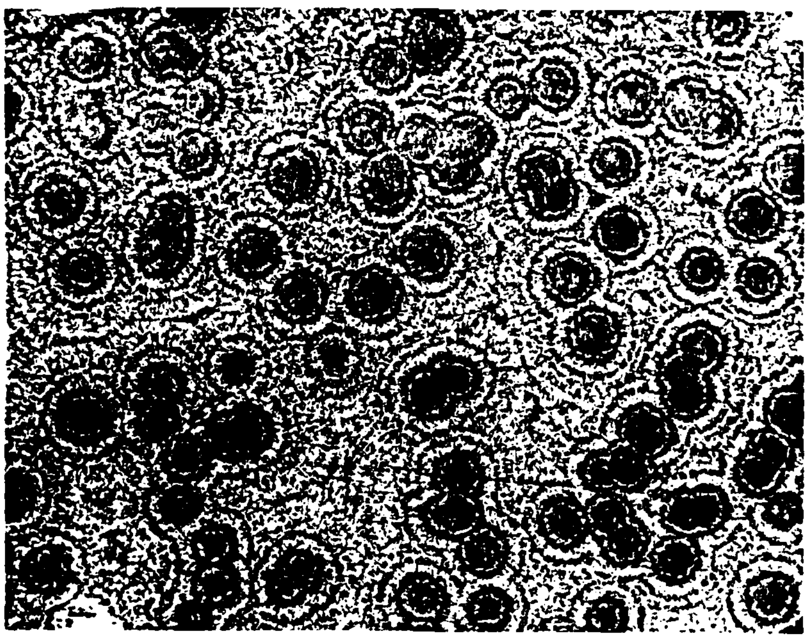
100X Magnification

Both were flat plate runs: 1400 °C
Pressure = 5mmHg
4 CFH Hydrogen
Hydrogen:MTCS=2.0

1(A) Run 2005
1(B) Run 2007



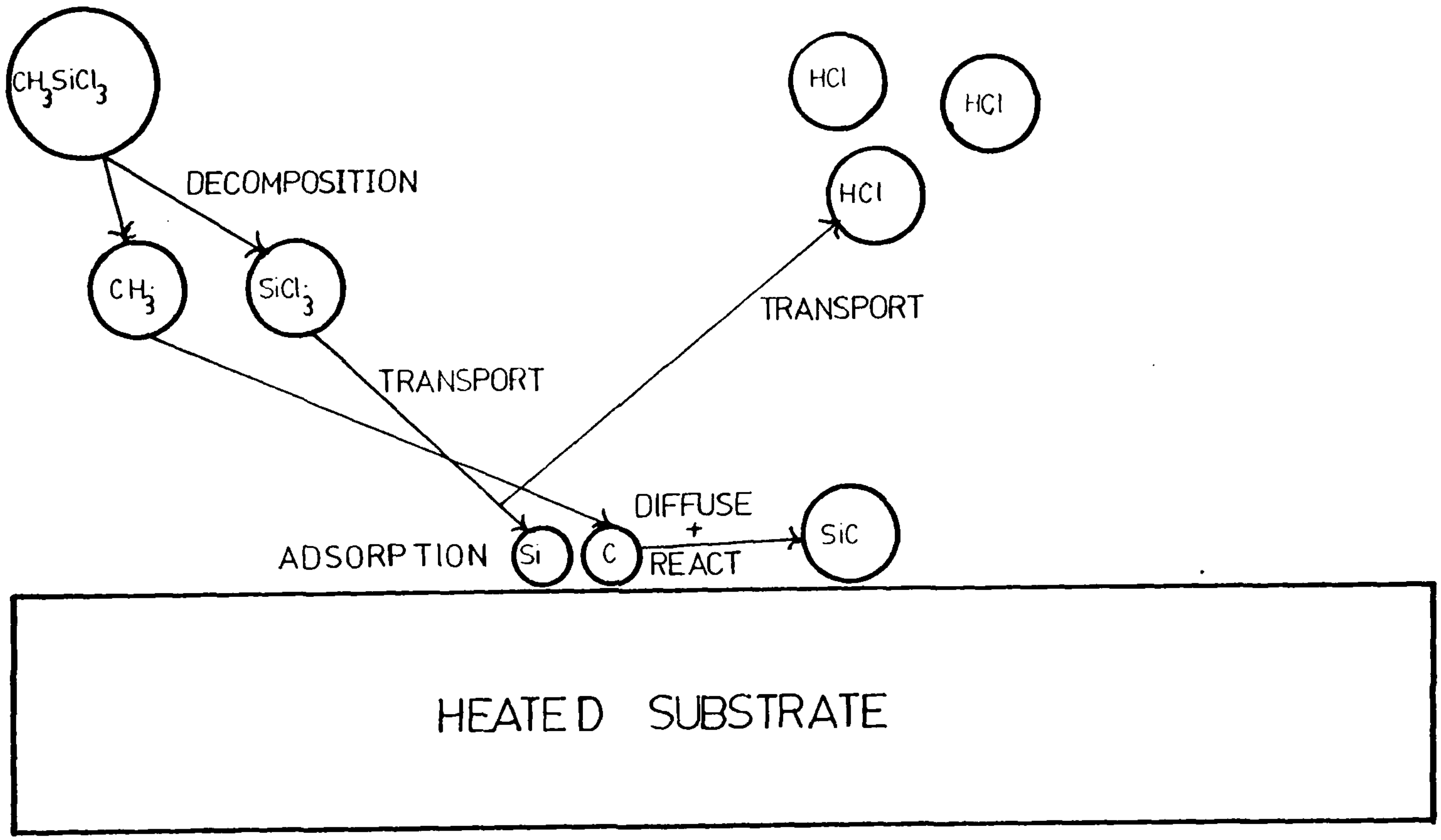
(A)



(B)

Figure 2

Decomposition of Methyltrichlorosilane



CH3SiCl3
DECOMPOSITION
CH3
SiCl3
TRANSPORT
HCl
HCl
HCl
TRANSPORT
ADSORPTION
Si
C
DIFFUSE
+
REACT
SiC
HEATED SUBSTRATE

Figure 3

Decomposition of MTCS after Cartwright[11]

$$\begin{array}{c} \quad\ \mathrm{H} \quad \mathrm{Cl} \\ \quad\ | \qquad | \\ \mathrm{H-C-Si-Cl} \\ \quad\ | \qquad | \\ \quad\ \mathrm{H} \quad \mathrm{Cl} \end{array} \rightleftharpoons \cdot CH_3 + \cdot SiCl_3$$

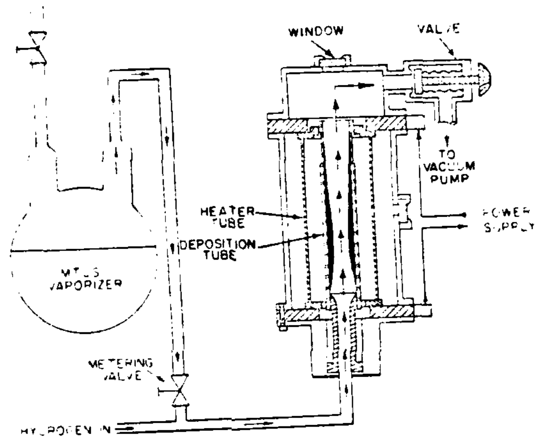
$$\cdot CH_3 \rightleftharpoons C + 3H$$

$$\cdot SiCl_3 \rightleftharpoons SiCl_2 + Cl$$

$$SiCl_2 + H_2 \rightleftharpoons Si + 2HCl$$

$$Si + C \rightleftharpoons SiC$$

Figure 4
Schematic of Deposition Apparatus



WINDOW
VALVE
TO
VACUUM
PUMP
HEATER
TUBE
DEPOSITION
TUBE
POWER
SUPPLY
VAPORIZER
METERING
VALVE

Figure 5

Profiles for "Hot Wall" Deposition System

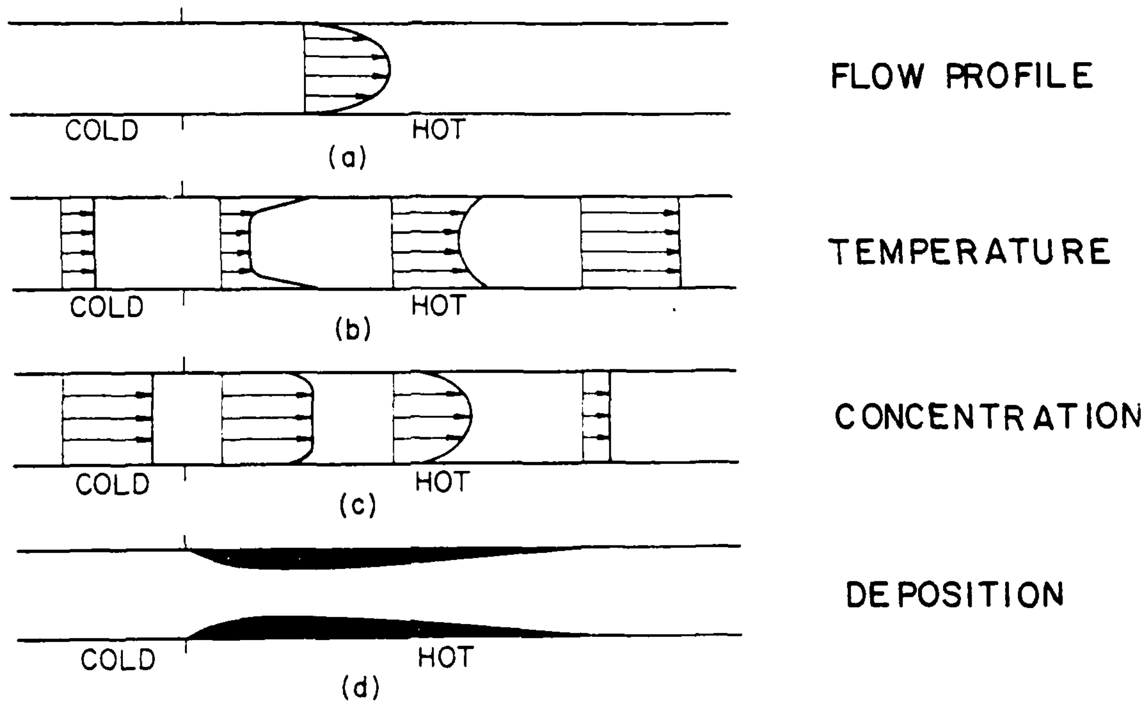

FLOW PROFILE
COLD
HOT
(a)
TEMPERATURE
COLD
HOT
(b)
CONCENTRATION
COLD
HOT
(c)
DEPOSITION
COLD
HOT
(d)

Figure 6

Deposition Profiles as a Function of Temperature

After Weiss[2]

DEPOSITION RATE PROFILES

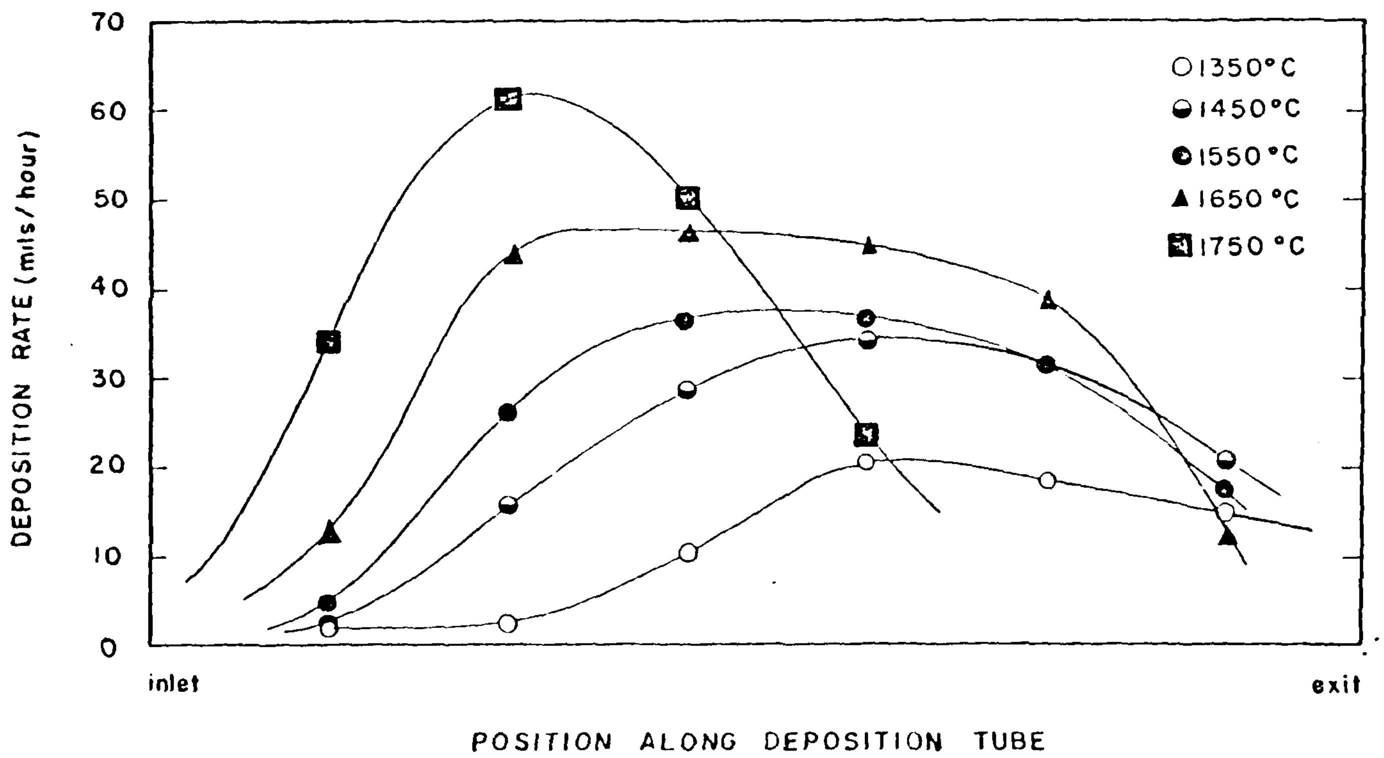


Figure 7

Deposition Profiles for Methyltrichlorosilane vs. Methyldichlorosilane

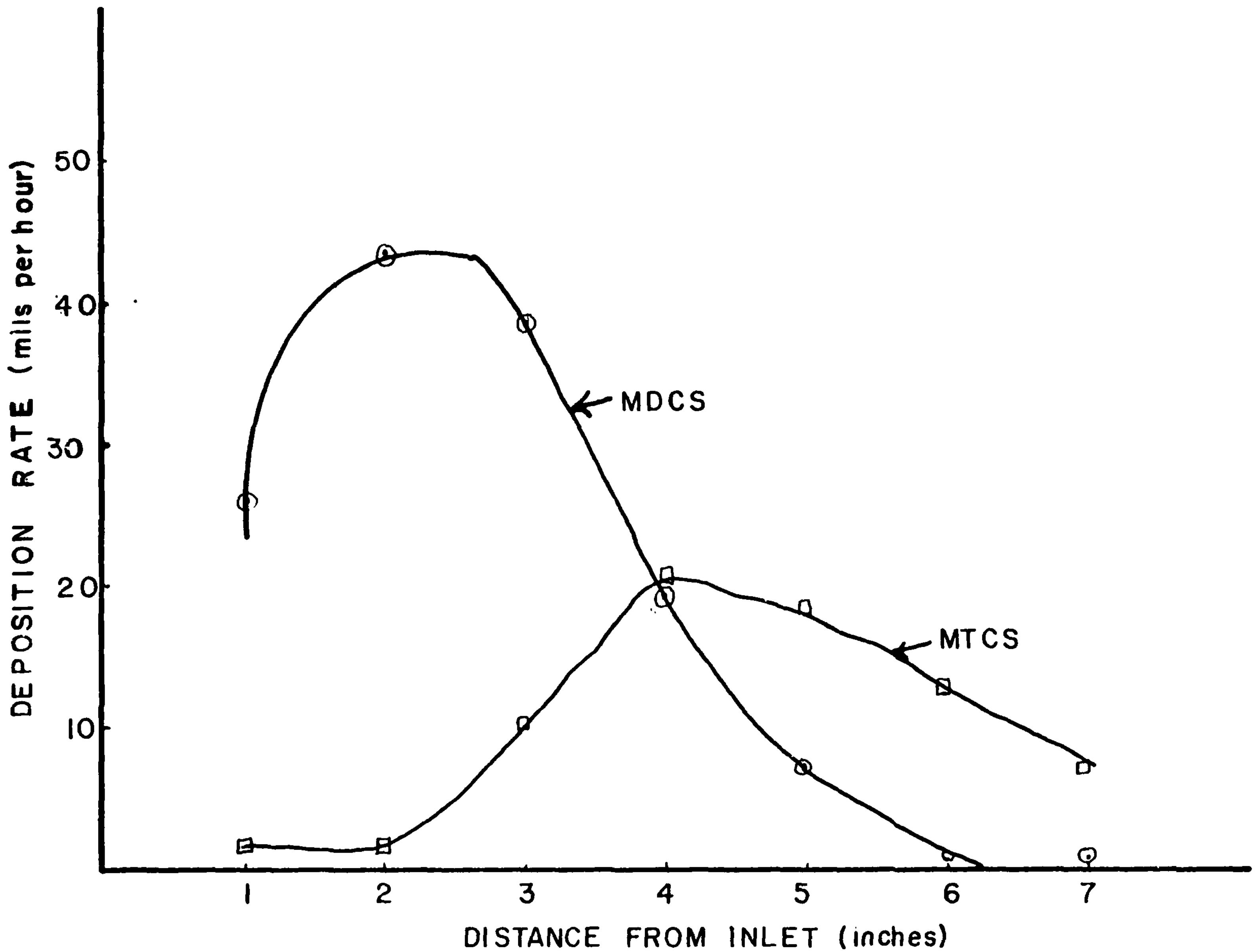
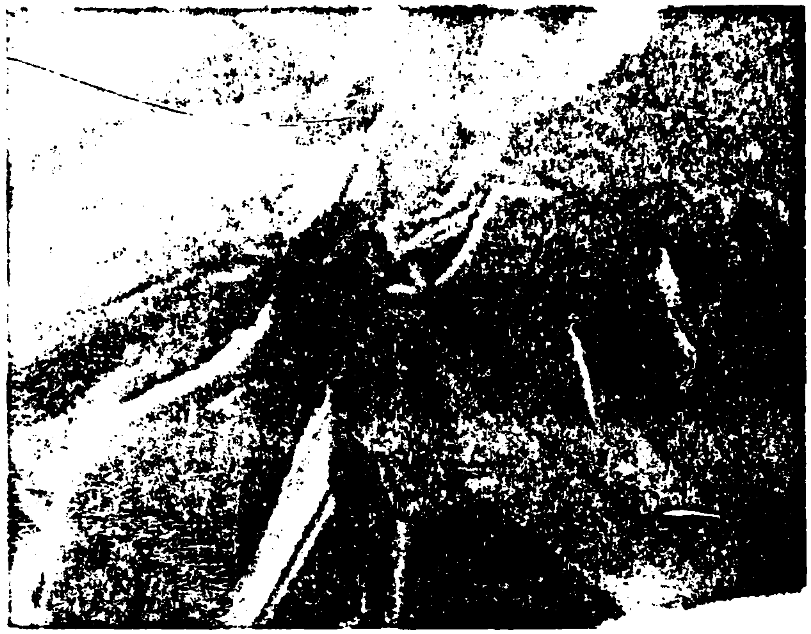

DEPOSITION RATE (mils per hour)
50
40
30
20
10
MDCS
MTCS
1
2
3
4
5
6
7
DISTANCE FROM INLET (inches)

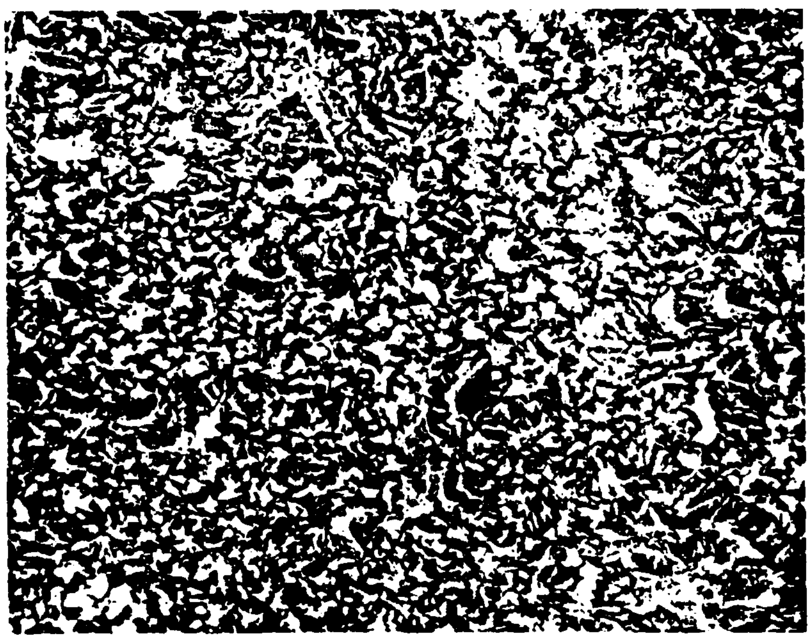
Figure 8

Effect of Temperature

Scanning Electron Micrographs 1000X



1650 °C

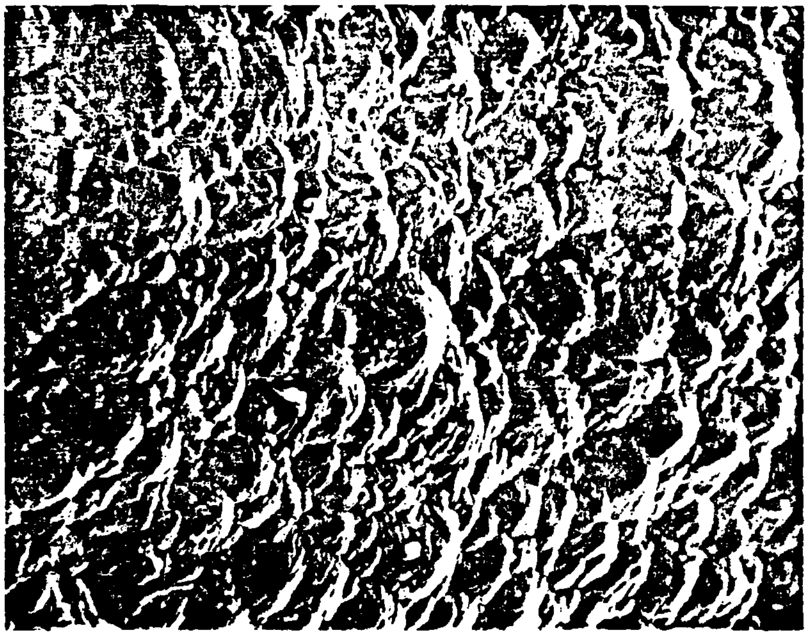


1450 °C

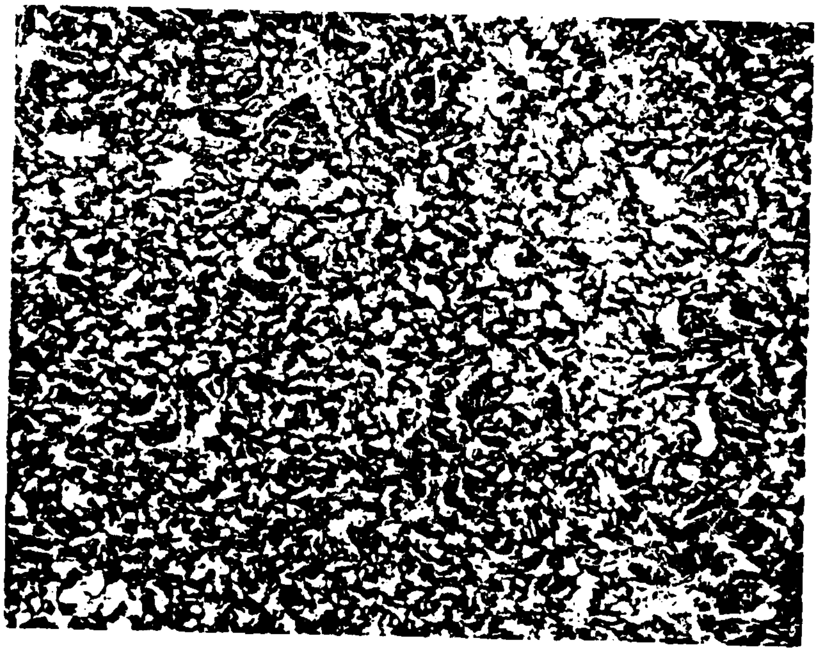
Figure 9

Effect of Concentration

Scanning Electron Micrographs 1000X



8:1 H_2:MTCS

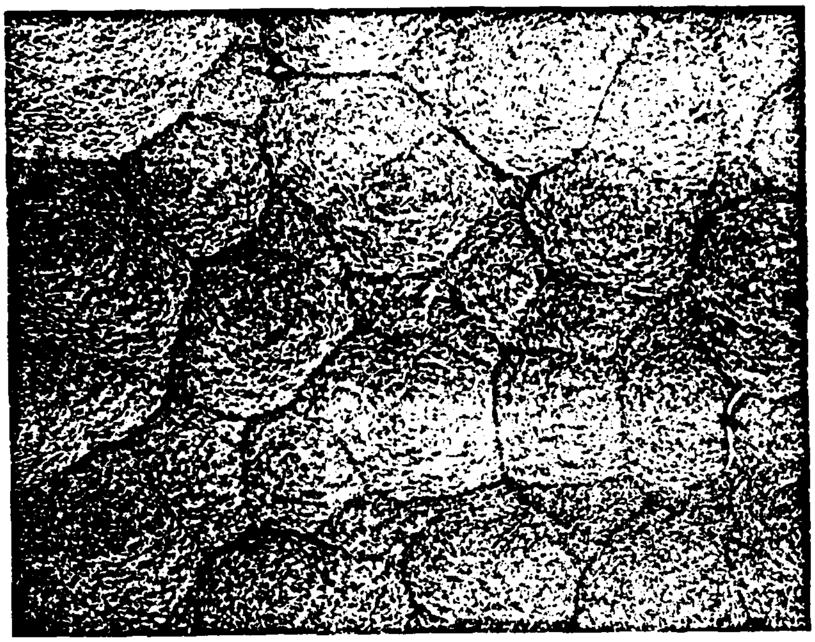


2:1 H_2:MTCS

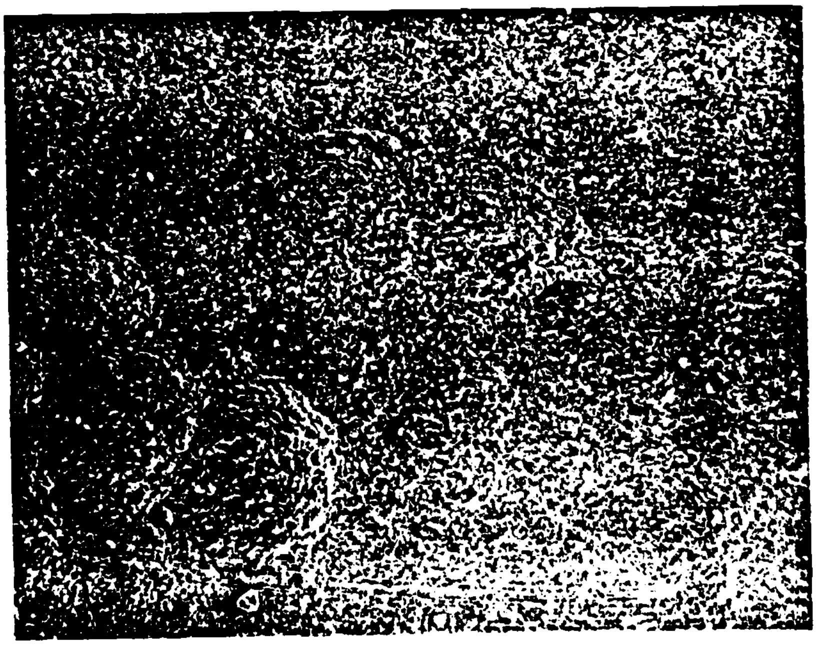
Figure 10

Effect of Pressure

Scanning Electron Micrographs 50X



20 mmHg



5 mmHg

Figure 11

Amount of Non-cubic Material as a Function of Temperature

2:1 Hydrogen to MTCS
Pressure=5mmHg
2 CFH Hydrogen
One-half inch bore tube

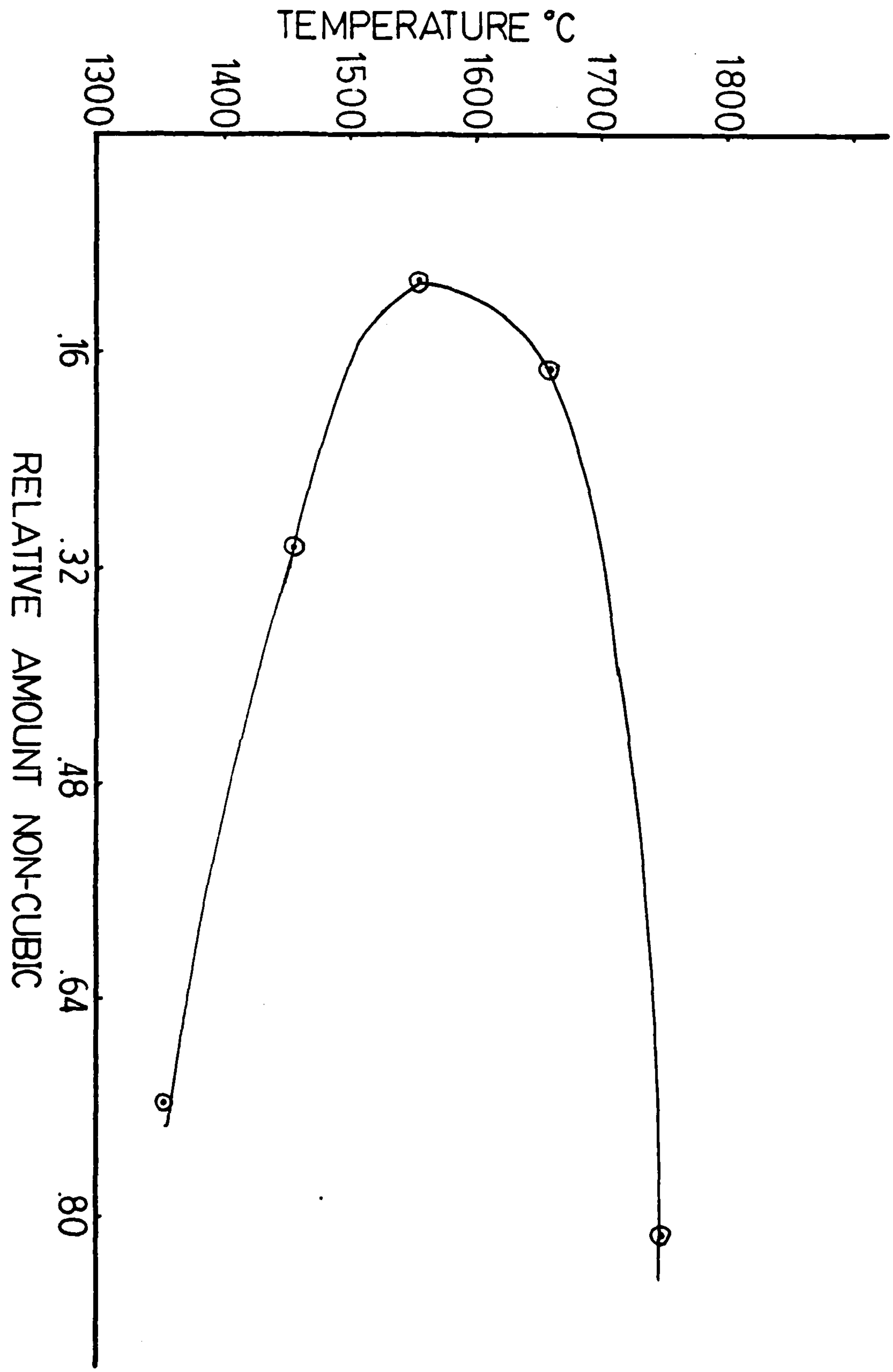

TEMPERATURE °C
1300
1400
1500
1600
1700
1800
RELATIVE AMOUNT NON-CUBIC
.16
.32
.48
.64
.80

Figure 12

Defect Theory of Residual Stresses

After Hoar and Arrowsmith[16]

12(A) Effect of Surface Vacancies

12(B) Effect of Surface Adsorbed Atoms

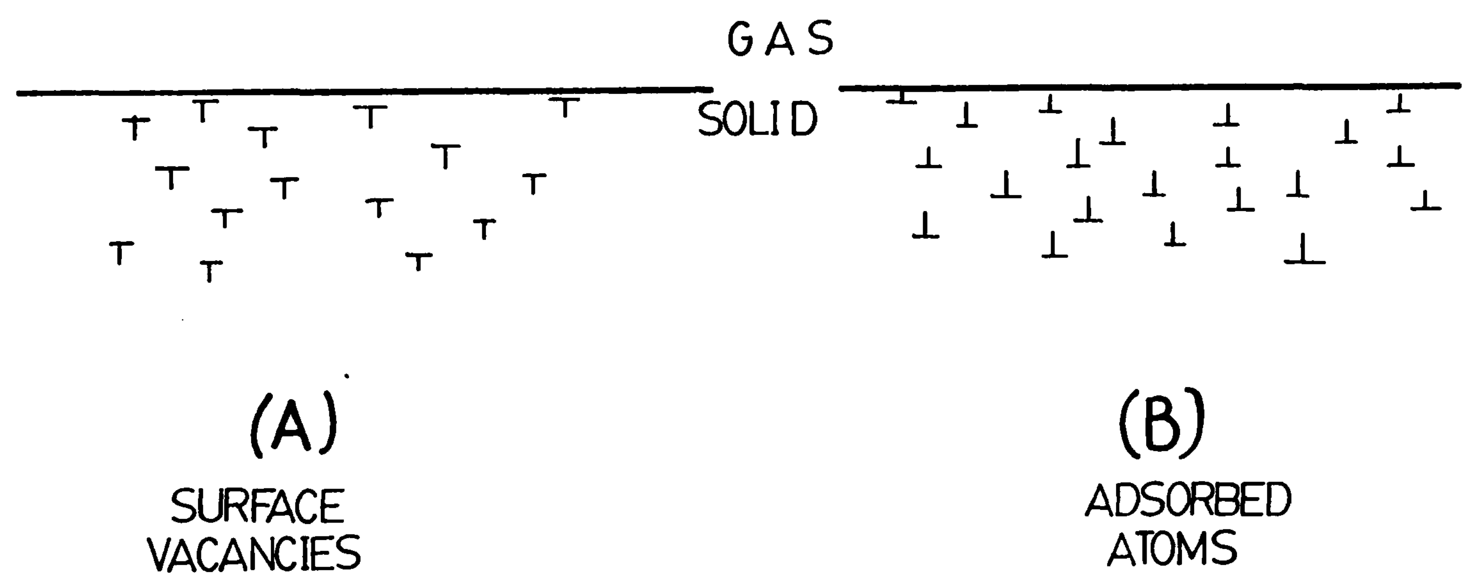

GAS
SOLID
(A)
SURFACE
VACANCIES
(B)
ADSORBED
ATOMS

Figure 13

Residual Stress vs. Thickness for a Flat Plate

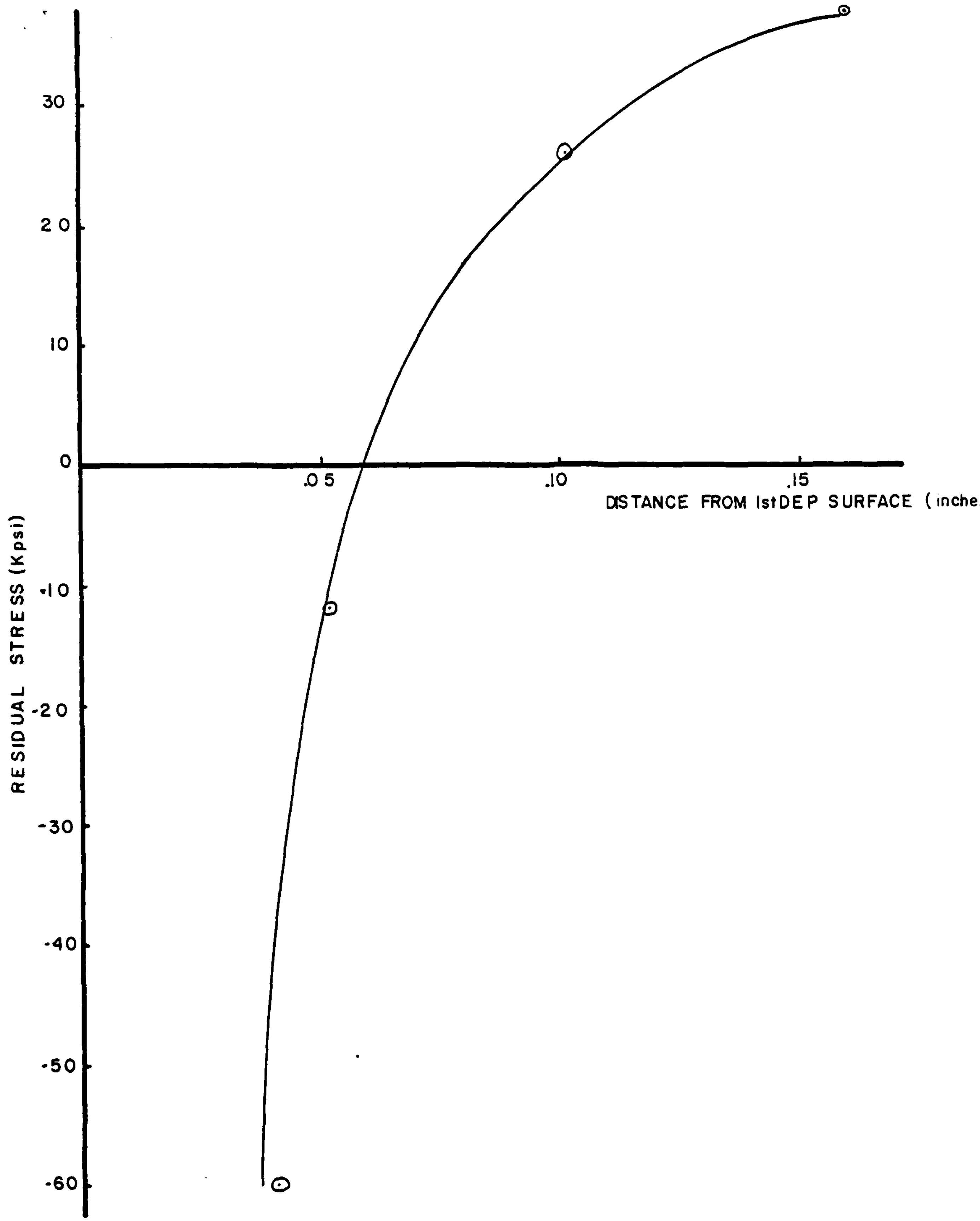
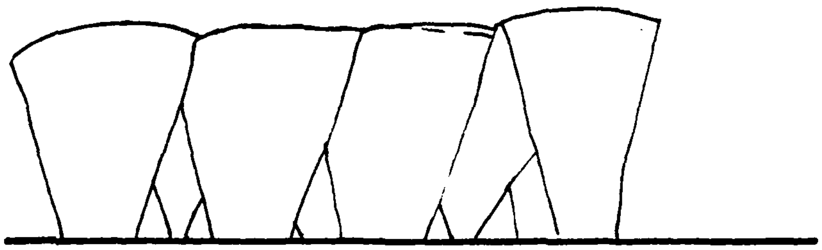

30
20
10
0
-10
-20
-30
-40
-50
-60
RESIDUAL STRESS (Kpsi)
.05
.10
.15
DISTANCE FROM Ist DEP SURFACE (inche.

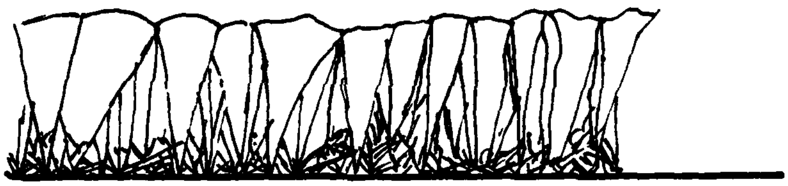
Figure 13A

(A) Coarsely Nucleated Structure.

(B) Finely Nucleated Structure.



COARSELY NUCLEATED



FINELY NUCLEATED

Figure 14

Preferred Orientation as a Function of Material Removed from the First-Deposited Surface

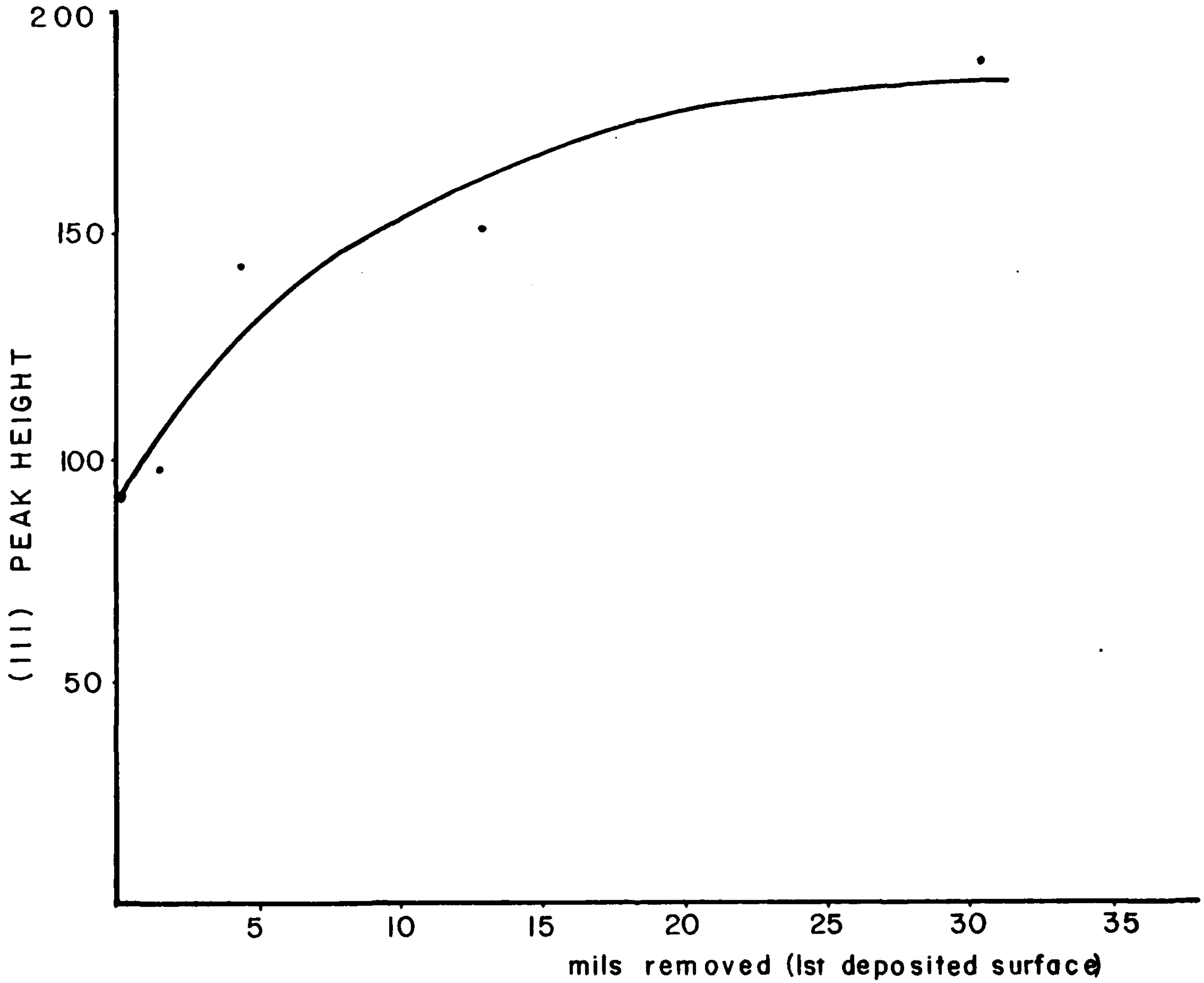

(111) PEAK HEIGHT
200
150
100
50
5
10
15
20
25
30
35
mils removed (lst deposited surface)

Figure 15

Sphere-like Material Found in a Poorly
Nucleated Deposit

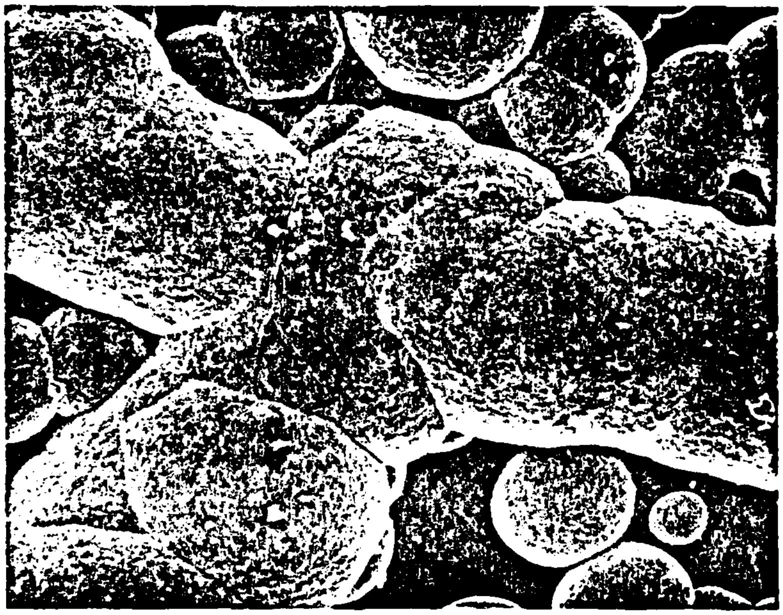
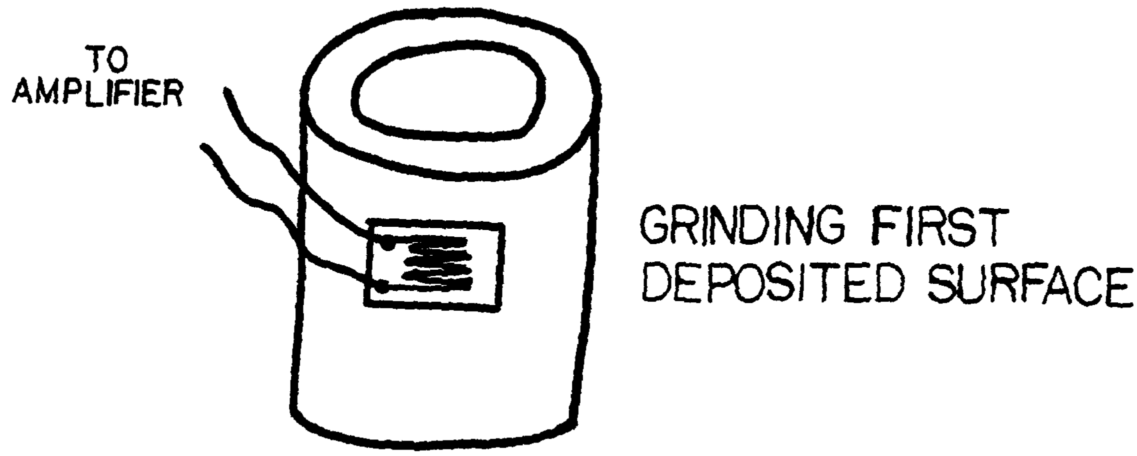
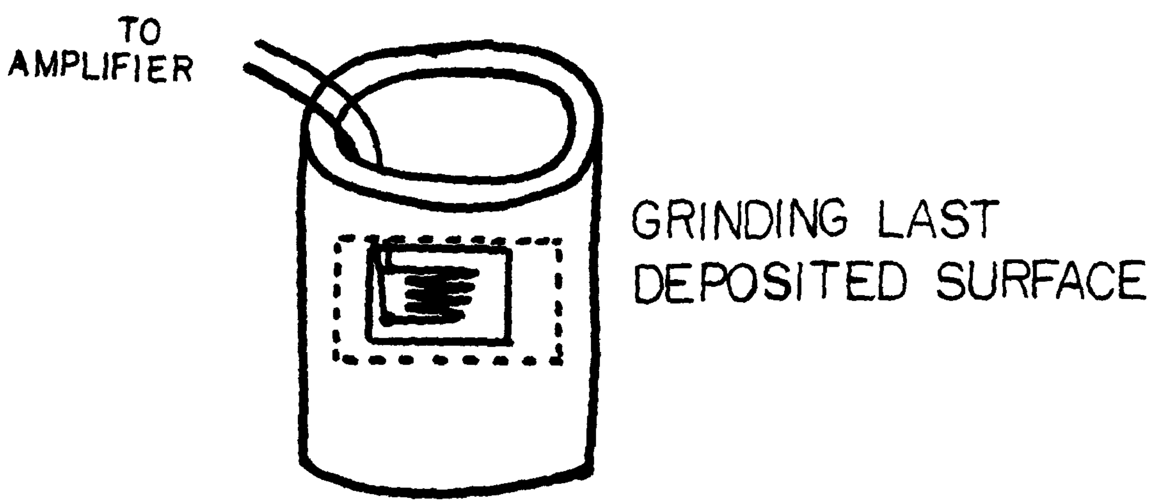


Figure 16

Measurement of strain in 1" cylinders of material to obtain residual stress data.


TO
AMPLIFIER
GRINDING FIRST
DEPOSITED SURFACE

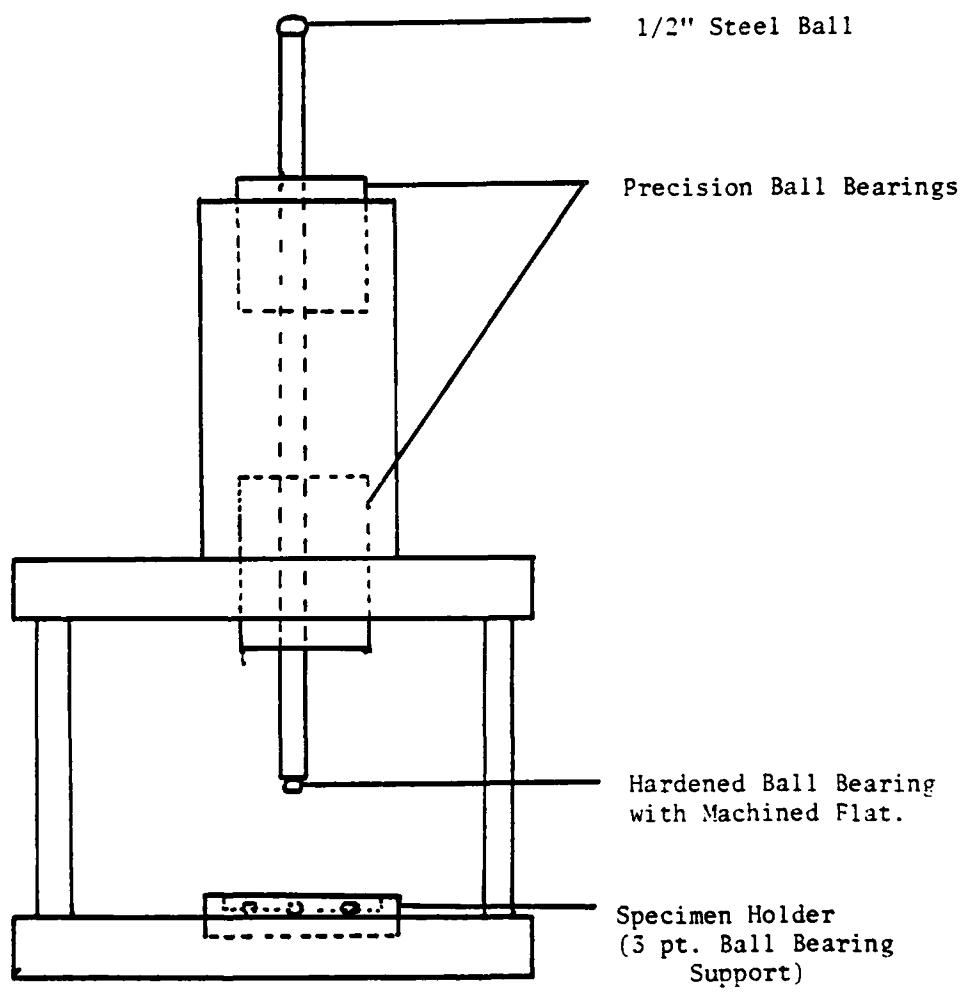
A


TO
AMPLIFIER
GRINDING LAST
DEPOSITED SURFACE

B

Figure 17

Biaxial Stress Measurement Assembly.


1/2" Steel Ball
Precision Ball Bearings
Hardened Ball Bearing with Machined Flat.
Specimen Holder (3 pt. Ball Bearing Support)